UNIFICATION OF COAL CHAR GASIFICATION REACTIONS

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INTRODUCTION

In the conversion of coal chars to gaseous fuels, the four important gasification reactions are:

$$C + O_2 \rightarrow CO \text{ and } CO_2$$

$$C + CO_2 \rightarrow 2\ CO$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + 2H_2 \rightarrow CH_4$$

We have studied extensively in this laboratory these reactions on coal chars produced from a complete spectrum of American coals from anthracite to lignite (1-4). For each reaction we have found a major increase in char reactivity with decreasing rank of the coal from which the char is produced. Such increase has been explained to be consistent with the three important parameters which control gasification rates of microporous chars. That is, as chars are produced from coals of decreasing rank under fixed conditions of charring, the concentration of carbon sites active to gasification increases, the accessibility of reactant gases to these active sites increases, and the specific activity of inorganic impurities towards catalysis of gasification increases.

In calculating reactivities in the past we have used the simple expression

$$R = \frac{1}{w} \cdot \frac{dw}{dt}$$

where either w is the starting weight of dry, ash-free char and dw/dt is the maximum value found as burn-off proceeds or w represents char weights remaining at various values of time t and dw/dt represents slopes at corresponding times such that R is found to be constant over some burn-off range. It was noted that even though there were major differences in char reactivity (R) as the rank of the parent coal from which chars were produced was changed, the shape of the burn-off versus reaction time plots appeared to be quite similar. If this is so, all reactivity plots should be able to be normalized using an adjustable time parameter, τ, which can conveniently be used as a measure of differences in reactivity for a wide spectrum of chars. This paper concerns itself with examining the feasibility of such a normalizing procedure.

EXPERIMENTAL

Char Preparation U. S. coals varying in rank from anthracite to lignite of 40x100 mesh size were used for the preparation of chars. Information on the coals is given in Table 1. The coals were heated in a N_2 atmosphere at a rate of 10°C/min to 1000°C and held for 2 hr.

Reactivity Measurements Burn-off versus time plots were determined for various chars in air (1 atm) at 405°C, CO_2 (1 atm) at 900°C, steam (.022 atm) at 910°C, and H_2 (27.2 atm) at 980°C. Under these conditions, mass transport resistance to diffusion of reactants down through the shallow bed of char particles (about 3mg)

had a negligible effect on gasification rates; gasification rates could be conveniently measured by weight loss using TGA.

RESULTS AND DISCUSSION

The principle of normalizing reactivity plots is shown in Figures 1 and 2. Figure 1 shows burn-off versus time plots for the lignite char, PSOC-91, reacted in various partial pressures of O_2 at a total O_2-N_2 pressure of 1 atm. As expected, the gasification rate decreases sharply with decreasing O_2 pressure. Figure 2 shows that these individual reactivity plots can be well normalized using a dimensionless time scale such that $t/\tau_{0.5}$ equals one at a fractional burn-off of 0.5. Values of $\tau_{0.5}$, or the times to reach a fractional burn-off of 0.5, decrease from 61.0 min to 14.8 min as the percentage O_2 in the reactant mixture is increased from 2 to 21%.

Figure 2 is more or less typical of the shape of burn-off versus $t/\tau_{0.5}$ plots found for all chars reacted in all gases. That is, at low values of $t/\tau_{0.5}$ there is an increase in slope of the plot, as $t/\tau_{0.5}$ increases. The plot then goes through a maximum in slope, followed by a lengthy region of slowly decreasing slope as fractional burn-off approaches one. Qualitatively, at this time, plots of this shape can be explained on the basis of what is known about the development of porosity and surface area in microporous chars as they undergo gasification. Before gasification, these chars contain closed porosity, that is porosity inaccessible even to helium. With the onset of gasification, two important phenomena occur: i) enlargement of pores that were open in the unreacted char and ii) opening up of closed pores. Since the total number of pores is increased as well as their average radius, specific pore volume and specific surface area increase with increasing carbon burn-off. The specific surface area increases sufficiently rapidly as $t/\tau_{0.5}$ increases that the product of specific area and char weight remaining, that is total area remaining, increases. The result is an increasing slope of the burn-off versus $t/\tau_{0.5}$ plot. At some point, depending upon the pore structure of the individual char, walls between existing pores are gasified away; and the total number of open pores commences to decrease. This leads to specific pore volume and specific surface area ultimately going through maxima as burn-off proceeds. It leads then to the slope of the burn-off versus $t/\tau_{0.5}$ plot going through a maximum value as burn-off proceeds.

This qualitative picture ignores the effect which catalysis by inorganic impurities can have on the shape of the burn-off curve. For example, if a catalyst is initially very active but as burn-off proceeds becomes less active because of sintering or change in chemical state, the $t/\tau_{0.5}$ region over which the gasification rate is increasing can be shortened or indeed removed completely. That is, the maximum rate can be observed immediately as gasification commences. In this case, the catalytic effect on gasification is obviously overshadowing the effect of increase in specific pore volume and specific surface area.

With these points in mind, it is of interest to see the extent to which one equation, with $\tau_{0.5}$ being the only adjustable parameter, can unify all the char reactivity data obtained in this paper.

Computer correlation of data for each gasification medium was conducted, as well as computer correlation of data for all gasification media. Burn-off versus time data for a fractional burn-off up to 0.7 were used in all cases. The suitability of the following equations to correlate the data was tested: a linear equation between burn-off and $t/\tau_{0.5}$, an equation involving first and second power terms in $t/\tau_{0.5}$, an equation involving first and third power terms in $t/\tau_{0.5}$, and an equation involving first, second, and third power terms in $t/\tau_{0.5}$. The latter equation gave the best correlation of the data.

Tables 2 and 3 summarize the results. For the char produced from coal PSOC-140, ten reactivity runs were made with steam. For the ten determinations, a 95% confidence interval on the mean value of $\tau_{0.5}$ is ±0.8. Table 2 shows the wide variation of $\tau_{0.5}$ values found for the chars in each reaction medium as the rank of coal from which the chars were produced changes. Generally, $\tau_{0.5}$ values for each reactant gas fall in the same order, but there are exceptions, as expected, which reflect the uniqueness of each reaction. For example, values of specific catalytic activity of impurities for each reaction are not expected to fall in the same order.

Table 3 presents the best values for coefficients in the cubic equations between fractional burn-off and $t/\tau_{0.5}$ for each reactant, as well as for all reactants. R^2 values give how much of the sum of variance, assuming no correlation between burn-off and $t/\tau_{0.5}$, can be removed by the particular cubic equation. It is obvious that for each individual reactant and also for all reactants the equations given result in a high correlation of results for burn-off versus $t/\tau_{0.5}$.

As discussed earlier, each char-reactant gas mixture shows some region of $t/\tau_{0.5}$ over which the reaction rate is first order in amount of char remaining. Thus computer correlations were also made with the first order model, $\ell n[1/(1 - BO)] = k(t/\tau)$, where BO is fractional burn-off. These results are also summarized in Table 3. If the data perfectly obeyed the first order model, k must equal 0.69 since $t/\tau_{0.5} = 1.0$ at BO = 0.5. Different reactions are seen to be more or less closely described, over a fractional burn-off range up to 0.7, by a first order equation. A reasonably good correlation is found for the C-air reaction, and a low correlation is found for the C-CO_2 reaction.

The success of the cubic equation to further correlate reactivity data was studied for other reaction conditions. It was successful in correlating data for the char-steam reaction as the partial pressure of steam and reaction temperature were varied.

From these studies, it is concluded that a good parameter to use to correlate char reactivity data is the time required to reach a fractional burn-off of 0.5. When this parameter is used, it is also shown that all of our char gasification data can be successfully normalized into burn-off versus $t/\tau_{0.5}$ plots of almost similar shape. Since char reactivity runs also exhibit a $t/\tau_{0.5}$ region where rate is first order in weight of char remaining, it probably is desirable to give first order rate constants for each run over the particular $t/\tau_{0.5}$ region in order to adhere to the more conventional treatment of kinetic data.

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REFERENCES

1. Jenkins, R. G., Nandi, S. P., and Walker, P. L., Jr., Fuel, 52, 288 (1973).

2. Hippo, E. and Walker, P. L., Jr., Fuel, 54, 245 (1975).

3. Tomita, A., Mahajan, O. P., and Walker, P. L., Jr., "Reactivity of Heat-Treated Coals in Hydrogen", Fuel, communicated.

4. Linares, A., Mahajan, O. P., and Walker, P. L., Jr., "Reactivities of Heat-Treated Coals in Steam", ACS Fuel Chemistry Division Preprints, New Orleans, March, 1977.

TABLE 1 - COALS USED TO PRODUCE CHARS

PSOC Sample No.	ASTM Rank	State	Ash, % (dry)	C	H	N	Org S
89	Lignite	N.D.	11.6	63.3	4.7	0.48	0.98
91	Lignite	Mon.	7.7	70.7	4.9	0.80	0.30
87	Lignite	N.D.	8.2	71.2	5.3	0.56	0.46
140	Lignite	Tex.	9.4	71.7	5.2	1.30	0.72
138	Lignite	Tex.	10.3	74.3	5.0	0.37	0.51
98	Sbb. A	Wyo.	8.4	74.3	5.8	1.20	1.1
101	Sbb. C	Wyo.	6.1	74.8	5.1	0.89	0.30
26	HVB	Ill.	10.8	77.3	5.6	1.10	2.3
22	HVC	Ill.	10.1	78.8	5.8	1.60	1.8
24	HVB	Ill.	11.8	80.1	5.5	1.10	2.3
67	HVB	Ut.	4.8	80.4	6.1	1.30	0.38
171	HVA	W.Va.	7.6	82.3	5.7	1.40	1.8
4	HVA	Ky.	2.1	83.8	5.8	1.60	0.66
114	LV	Pa.	9.8	88.2	4.8	1.20	0.62
81	Anthracite	Pa.	7.8	91.9	2.6	0.78	0.54
177	Anthracite	Pa.	4.3	93.5	2.7	0.24	0.64

TABLE 2 - $\tau_{0.5}$ VALUES FOR GASIFICATION RUNS

PSOC Sample No.	$\tau_{0.5}$ for Different Reacting Gases, min			
	Air	Steam	CO_2	H_2
89	-	-	5.5	43.5
91	14.8	10.6	5.0	36.5
87	30.0	11.4	-	24.0
140	29.6	19.6	10.3	34.0
138	69.5	28.0	17.0	32.0
98	66.4	-	26.0	50.0
101	21.6	13.6	7.0	37.5
26	121	138	200	59.0
22	99.0	64.0	54.0	33.5
24	78.5	51.0	30.0	32.0
67	134	152	220	34.5
171	-	260	-	96.0
4	-	114	-	49.0
114	-	-	-	126
81	-	255	270	51.5
177	-	330	-	110

TABLE 3 - UNIFICATION OF COAL CHAR GASIFICATION REACTIONS

Reactant	No. of Chars	Cubic Model				First Order	
		a	b	c	R^2	Slope	R^2,%
Air	10	0.317	0.367	-0.182	96.0	0.756	94.1
CO_2	11	0.436	0.189	-0.122	99.2	0.728	78.4
H_2O	13	0.375	0.276	-0.148	99.1	0.761	87.4
H_2	16	0.349	0.283	-0.144	96.6	0.693	88.6
All	50	0.368	0.277	-0.147	98.2	0.727	87.5

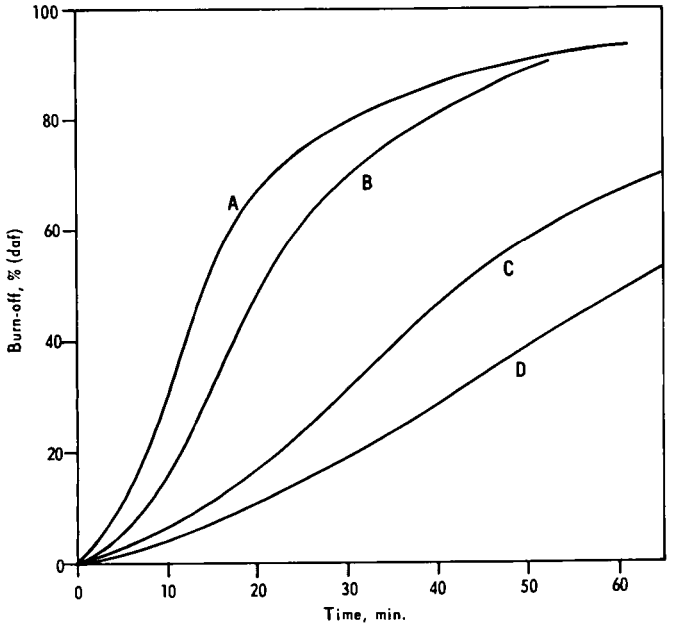

Figure 1. Influence of oxygen concentration on reactivity of PSOC-91 char at 405°C. A, 21% O_2; B, 10% O_2; C, 4% O_2; D, 2% O_2.

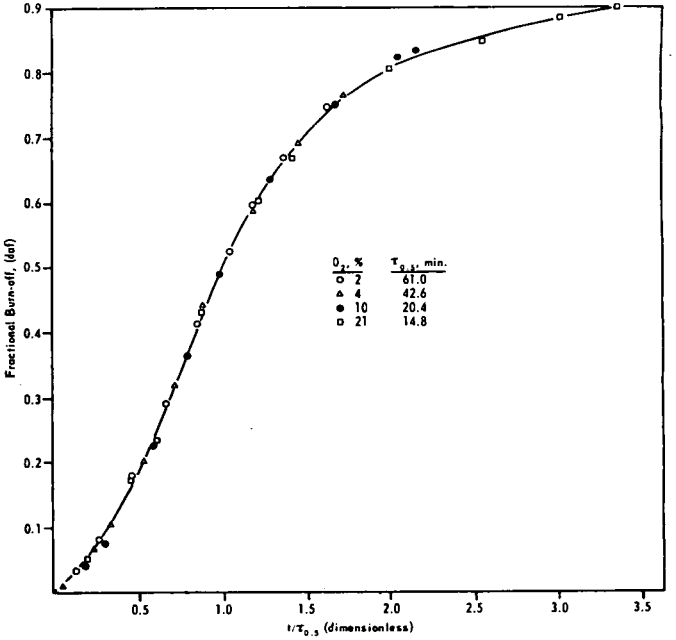

Figure 2. Normalized plot for reaction of PSOC-91 char at 405°C in different concentrations of O_2.